Measurements of Cayuga Lake Production

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In Partial Fulfillment of the Requirements for the Degree of Master of Engineering

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Abstract

This study aims to compare estimates of primary productivity in Cayuga Lake based on *in situ* measurements of dissolved carbon dioxide (CO_2) and dissolved oxygen (DO). Historically, productivity was estimated using the light/dark bottle method. More recent procedures have used *in situ* DO measurements. However, DO is a by-product of production. Directly using CO_2 to determine productivity could offer a faster and more accurate result. Four locations at the southern end of Cayuga Lake were sampled between July 3, 2012 and October 9, 2012. Free aqueous CO_2 was measured using an OxyGuard Dissolved CO_2 meter. Citric acid was added to the water sample to lower the pH to the range of 3-4, so that most of the inorganic carbon would be in the CO_2 form. Additionally, DO readings were taken using a Hydrolab DS 5. Average diel differences in CO_2 and DO were found at each of the four sampling sites. To evaluate production, diel DO concentrations were corrected for atmospheric diffusion. In addition, diel CO2 differences were assumed to be adequate measures of production. Direct ambient CO_2 concentration differences were found to have a strong, linear relationship with net ecosystem production.

Background

The objective of this study is to compare different methods of estimating primary production of Cayuga Lake through the use of *in situ* measurements of dissolved oxygen (DO) and dissolved carbon dioxide (CO_2). Traditionally, productivity has been estimated using DO, a by-product of production. This study wishes to directly analyze changes in CO_2 concentrations. Although this method is uncommon, it has been suggested that dissolved CO_2 values can be directly used to estimate production (Fahey, 2007). A productivity rate can be determined from the diel CO_2 concentration change, as well as the time interval between readings.

Site Description

This study was focused on the southern end of Cayuga Lake, one of the Finger Lakes located in western and central New York State. The eleven Finger Lakes were created by glacial ice and meltwater erosion approximately 15,000 years ago (Halfman 2006). Cayuga Lake is the second-largest of the Finger Lakes by volume. The lake is approximately 60 km long, with a maximum water depth of 132 meters. The surface area of the lake is approximately 172 km^2 (Mullins, 1998). The southern end of Cayuga Lake ranges from 1 meter to 40 meters in depth.

Measurements of pH vary seasonally, but are consistently found in the alkaline range. The highest pH range (8.5-8.85) can be found in surface waters during summer periods. These elevated pH levels can be attributed to increased algal photosynthetic

activity as carbon dioxide is incorporated into biomass. In deeper waters, pH values are typically between 7.2 and 7.9 (Genesee, 2000).

Carbonate System Chemistry

The carbonate system is comprised of the following species: aqueous carbon dioxide (CO_2), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}). The carbonate system controls the pH of many engineered and natural systems, such as freshwater lakes. Analytically, it is difficult to distinguish between the two species aqueous CO_2 and H_2CO_3. To overcome this difficulty, a new species $H_2CO_3^*$ is defined, which is the sum of $CO_{2\,(aq)}$ and H_2CO_3. This composite species is comprised predominantly (≈99.8%) of aqueous CO_2 (Lion, personal communication).

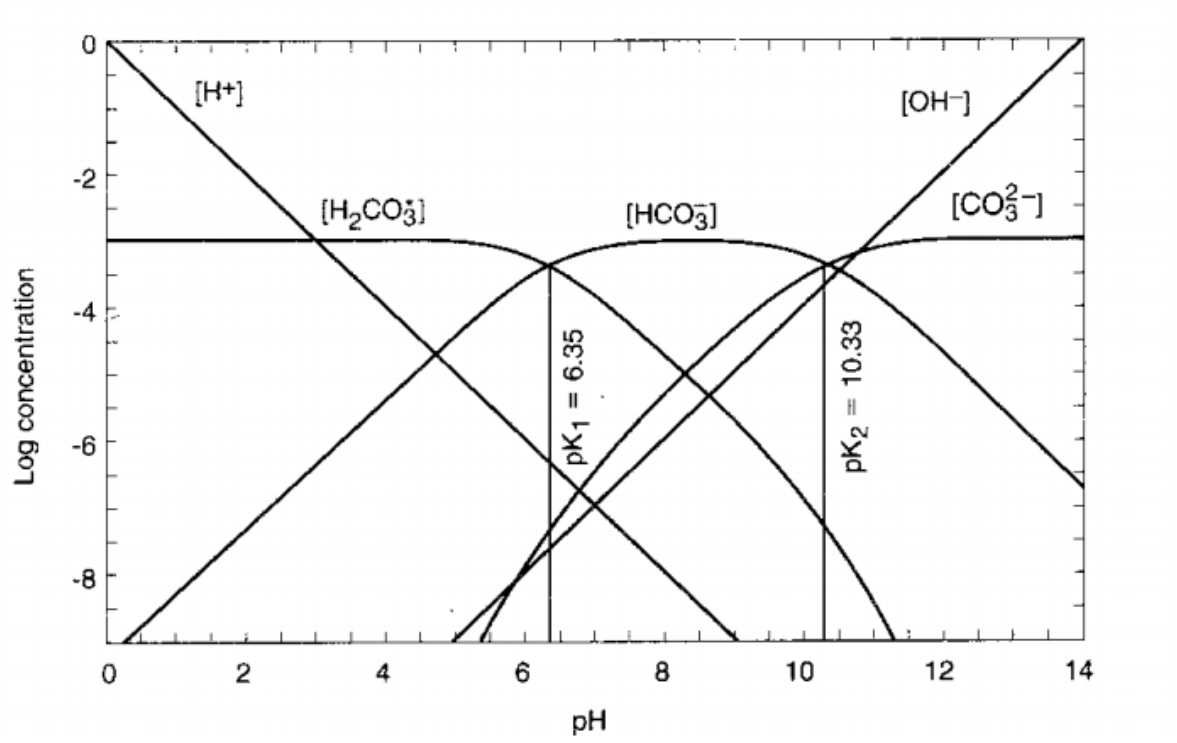

Figure 1 - Carbonate system species concentration vs. pH (Metcalf & Eddy, 2003).

Using relationships among charge balance, mass balance, and equilibria (such as ionization constants), a diagram depicting species concentrations versus pH can be constructed (Figure 1). One can determine the dominant carbonate species at a specific pH value. As Figure 1 depicts, acidic waters are indicative of high CO_2 and H_2CO_3 levels. High concentrations of CO_3^{2-} are present in basic waters. In the mid-range, between pH values of 6.3 to 10.3, similar to Cayuga Lake, the dominant species is HCO_3^-.

Lake Metabolism

Lake metabolism is governed by respiration and photosynthesis. Gross primary production (GPP) is the total fixation of inorganic carbon by photosynthesis. Theoretically, there should be a 1:1 molar ratio between CO_2 and O_2 as given by the general photosynthetic equation:

$$6\,CO_2 + 12H_2O + light \rightarrow C_6H_{12}O_6 + 6\,O_2 + H_2O$$

Respiration (R) is the process in which organisms break down complex organic substrates into inorganic carbon (CO_2). Net ecosystem production (NEP) represents the metabolic balance of the ecosystem; it is calculated by subtracting respiration from gross primary production (Cole 2000).

One of the most widely used methods to determine productivity is the light/dark bottle technique. Outlined by Vollenweider et al. (1969) for fresh water, this method is used to determine the rate that dissolved inorganic carbon is photosynthesized in the light. To conduct the experiment, a known amount of ^{14}C-CO_2 is added to both a clear and an opaque bottle containing the water sample. After a specific incubation period, the rate of photosynthesis can be found from the light bottle. The dark bottle represents the total amount of respiration (Peterson, 1980).

Different methods used for determining GPP and respiration can provide either overestimations or underestimations of productivity (Hanson, 2003). The light/dark bottle technique may underestimate GPP and respiration due to the method's reduced turbulence, unnatural light fields, and the respiration ^{14}C-labeled organic matter (Swaney, 1999). Additional studies have addressed issues with this method's extrapolation to whole-lake values (Hanson, 2003).

An alternative to bottle techniques is to measure *in situ* changes in free water DO. However, studies using diel DO in lakes are uncommon. Additionally, some studies have suggested an inadequate sensitivity in relatively unproductive waters. Swaney (1999) and Cole (2000) are two relatively recent studies that made use of *in situ* changes in DO concentration. Both studies believe that this method would prove more accurate than the bottle technique because natural light fields and natural turbulence would be maintained. This model is the basis for one component of the productivity analysis found later in this report.

Finally, it is proposed that *in situ* changes in dissolved CO_2 concentrations can be employed. This method would be a more direct and, theoretically, accurate approach to determine productivity. However, this method is complicated by changes in the distribution of the components of dissolved inorganic carbon (CO_2, H_2CO_3, $H_2CO_3^-$, CO_3^{2-}), as discussed above. As CO_2 is taken up by photosynthetic organisms, pH is expected to increase slightly. At a higher pH, more inorganic carbon is found in the bicarbonate form. If pH can be kept constant, or sampling accounts for this change, accurate CO_2 concentrations can be measured. This method has not yet been extensively

applied, but it could provide a direct way to estimate GPP, respiration, and NEP (Pace & Prairie, 2005).

Methods

Sampling Methods

All sampling was performed on the southern end of Cayuga Lake, closest to Ithaca, New York. Four sampling points, referred to as Inlet (N 42.455062°, W 76.511207°), D4 (N 42.46445°, W 76.50917°), F1 (N 42.47372°, W 76.51616°), and RUSS (N 42.47829°, W 76.52139°) were utilized (Figure 2). At each of these points, a Masterflex E/S Portable Sampler was used to collect a 100 mL water sample from approximately 3 meters beneath the water surface. The OxyGuard Dissolved CO_2 meter measures only dissolved CO_2 gas; it does not detect chemically bonded carbon dioxide or carbonates. As discussed in the *Background* section above, Cayuga Lake has a slightly basic pH of about 8.2, where most of the carbon exists in the bicarbonate (HCO_3^-) form. Therefore, 1 gram of citric acid crystals was added to the samples to decrease pH to a range of 3-4. At this pH range, the dominant species of the carbonate system is CO_2 and can be accurately measured by the OxyGuard sensor. This method was shown to not significantly alter true CO_2 concentrations (Nitzova, 2010).

In addition to the citric acid method mentioned above, a direct water column sample was measured for dissolved carbon dioxide. The OxyGuard CO_2 sensor was placed in the lake about 3 meters from the surface and was allowed to equilibrate in the water for approximately 15 minutes. A dissolved CO_2 reading was then taken. These readings should be less than those obtained through the citric acid method, because more of the inorganic carbon will be present in the bicarbonate form.

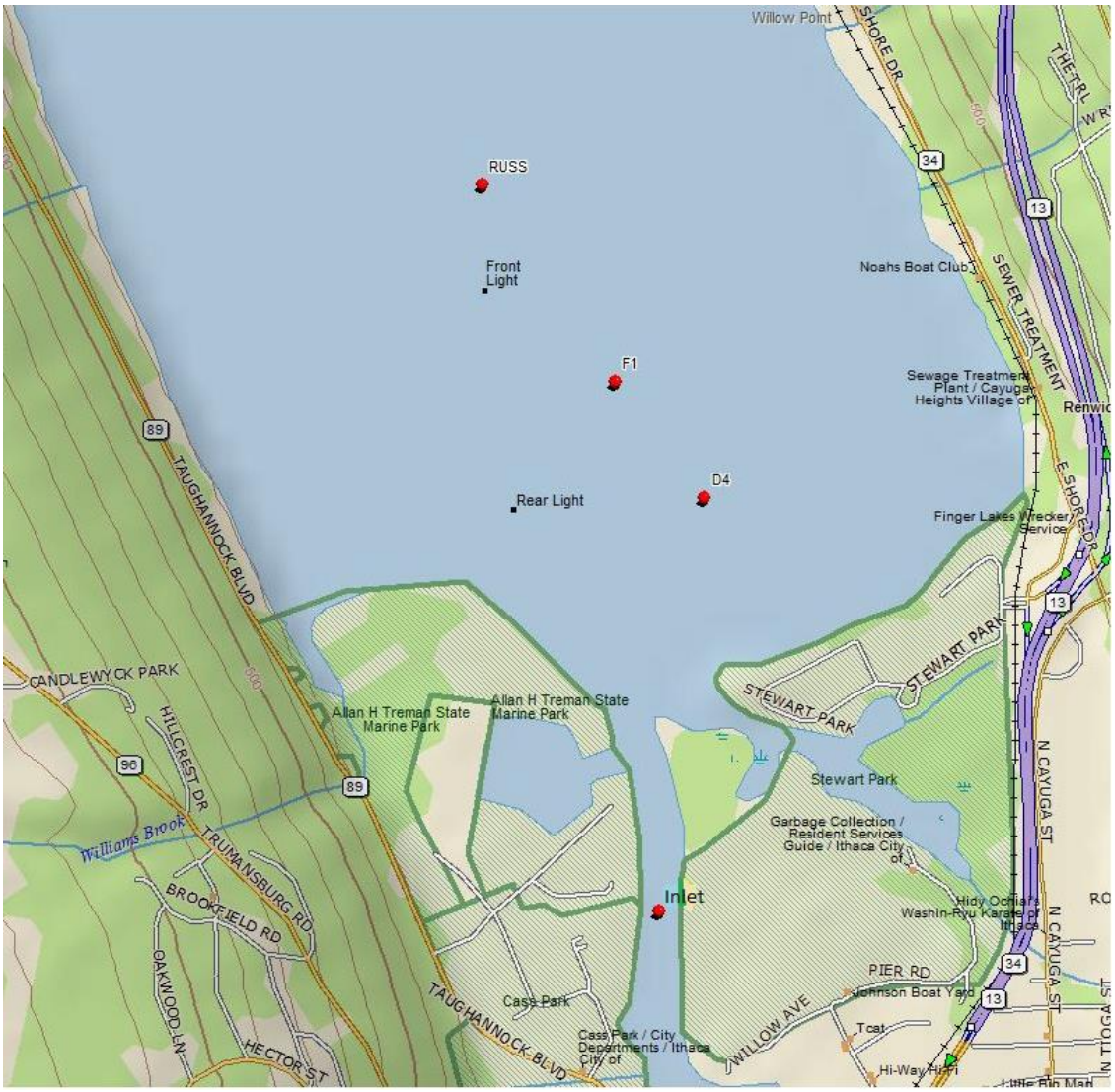

Figure 2 - Southern end of Cayuga Lake; the four sampling points (Inlet, D4, F1, and RUSS) are labeled.

Data were collected on nine different days from July 3, 2012 to October 9, 2012. Each day, samples were taken twice: once in the early morning near dawn and again in the mid-afternoon. Theoretically, dissolved carbon dioxide levels should be at its peak early in the morning, since organisms cannot perform photosynthesis without sunlight. The readings taken in the afternoon should report decreased carbon dioxide levels to represent the increased photosynthetic rate occurring during the day.

Additionally, the Hydrolab DS5 was used to collect information regarding temperature, dissolved oxygen, and pH. Carbon dioxide readings measured via the citric acid method are available for all nine sampling dates, while CO_2 values for the water column method are available for seven. Dissolved oxygen measurements were only taken on three sampling dates.

Productivity Analysis Methods

First, NEP was estimated from DO measurements, as adapted from Cole (2000) and Swaney (1999). The difference in DO concentrations between two time measurements were corrected for atmospheric diffusive exchange. The correction is a function of temperature and wind speed. Full equations and calculations can be found in Appendix II. The corrected DO difference represented the estimated NEP (mg O_2/L).

Second, NEP was estimated directly from the diel CO_2 difference. Only the three sampling dates for which DO data were available was used to compare this method to the NEP obtained from the DO concentrations.

Results

All raw sampling data can be found in Appendix I. From the raw data, one can see that all acidified CO_2 measurements were higher in magnitude than ambient concentrations at the same point. It is reassuring that the citric acid did sufficiently lower pH to convert most inorganic carbon to CO_2, thus increasing measured concentration. Paired ambient and acidified CO_2 measurements were positively correlated, with an R^2 value of 0.69 (Appendix 1, Figure 1).

Lake metabolism follows a diurnal cycle, in which theoretical maximum dissolved carbon dioxide levels occur just before dawn and minimum values occur just after dusk. Conversely, theoretical maximum dissolved oxygen concentrations occur just after dusk, while minimum values occur just before dawn. To model this, a paired diel dissolved CO_2 concentration was calculated by subtracting the afternoon values from the morning values (Figures 3 & 4). Conversely, paired DO concentrations were found by subtracting the morning values from the afternoon values (Figure 5).

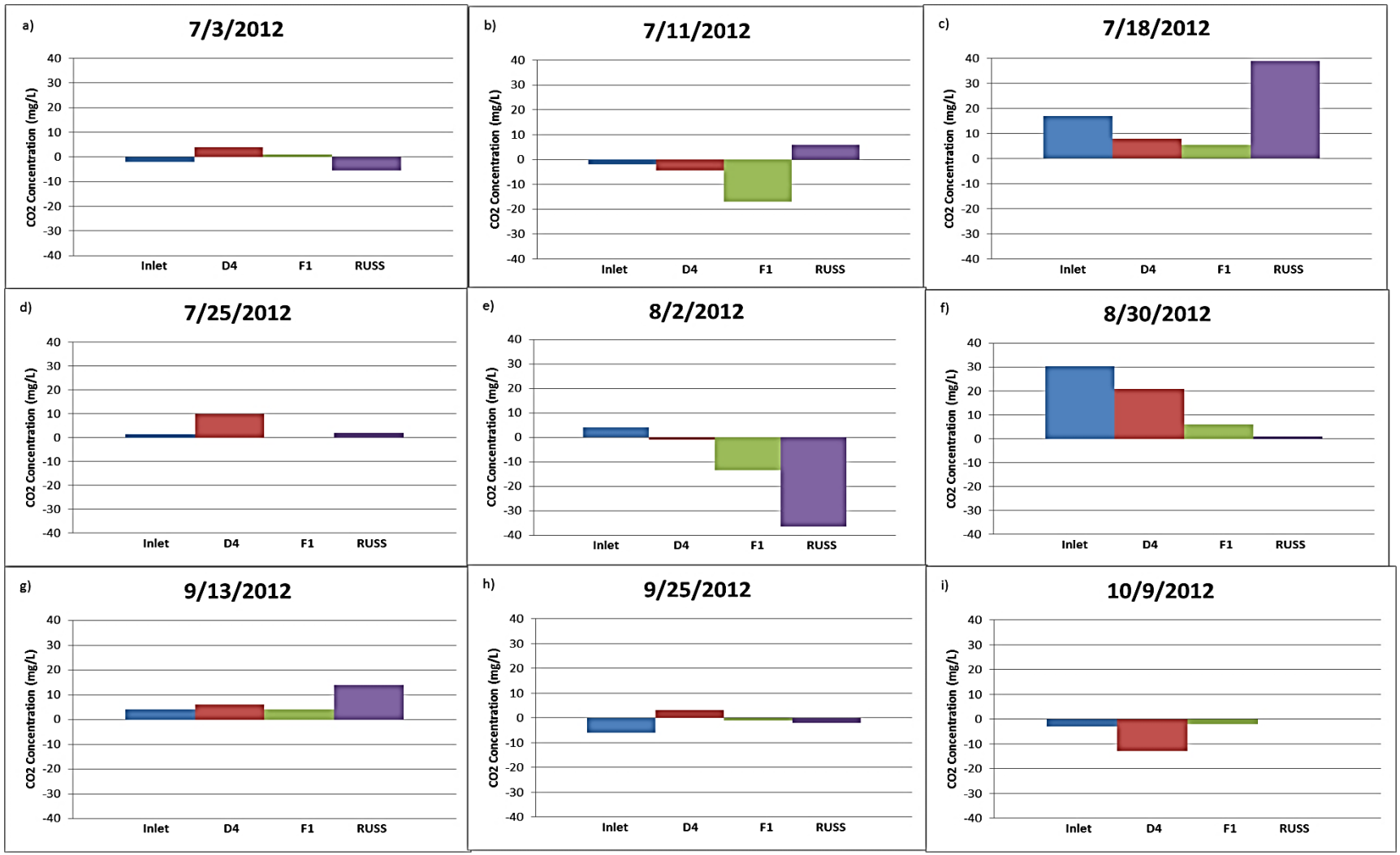

Figure 3 - Paired diel acidified dissolved CO_2 readings for the nine sampling dates at the four different sampling sites. All diel CO_2 measurements are reported in mg/L.

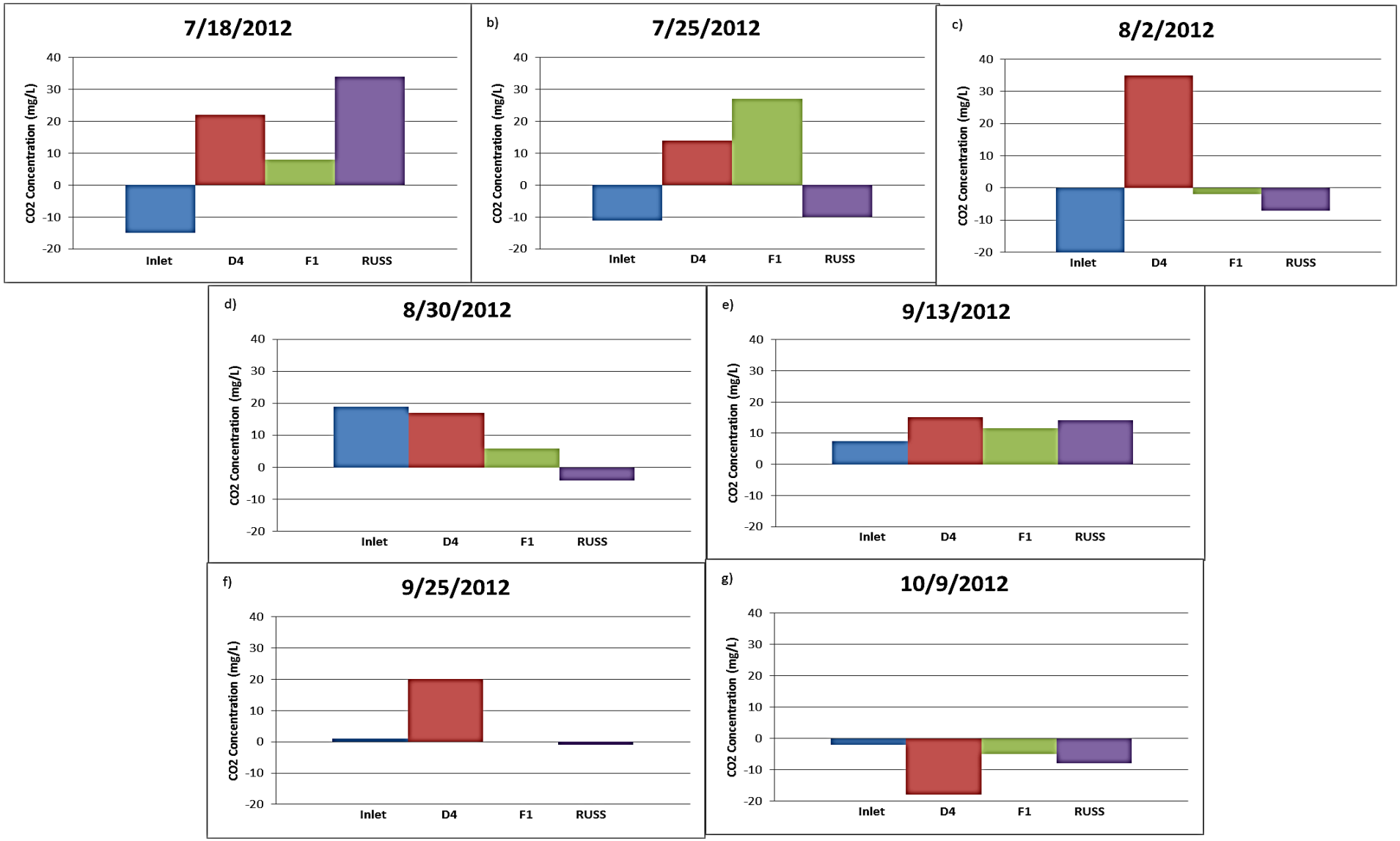

Figure 4 - Paired diel ambient dissolved CO_2 readings for the seven sampling dates at the four different sampling sites. All diel CO_2 measurements are reported in mg/L.

Figure 5 - Paired diel DO readings for the three sampling dates available at the four different sampling sites. All diel DO measurements are reported in mg/L.

Although environmental factors were variable across the sampling dates, an average value for diel carbon dioxide values was calculated for each of the sampling sites. This allowed us to compare productivity at each of the sites and observe any patterns within the dataset. The comparison of sites for dissolved CO_2 differences for the acidified and ambient concentrations can be seen in Figures 6 and 7, respectively.

The acidified diel CO_2 data (Figure 6) displays the greatest difference at the Inlet and D4 sampling sites. These two sites are the closest to the shore. The Inlet of the lake is silty, and does not have a substantial alga or macrophyte presence. One explanation for the large rate of production at the Inlet could be the influence of upstream waters. Incoming streams have a higher amount of algae, and could be contributing to the high production rate. The CO_2 concentration at F1 increases throughout the day, indicating that rate of respiration is greater than rate of photosynthesis at this sampling location.

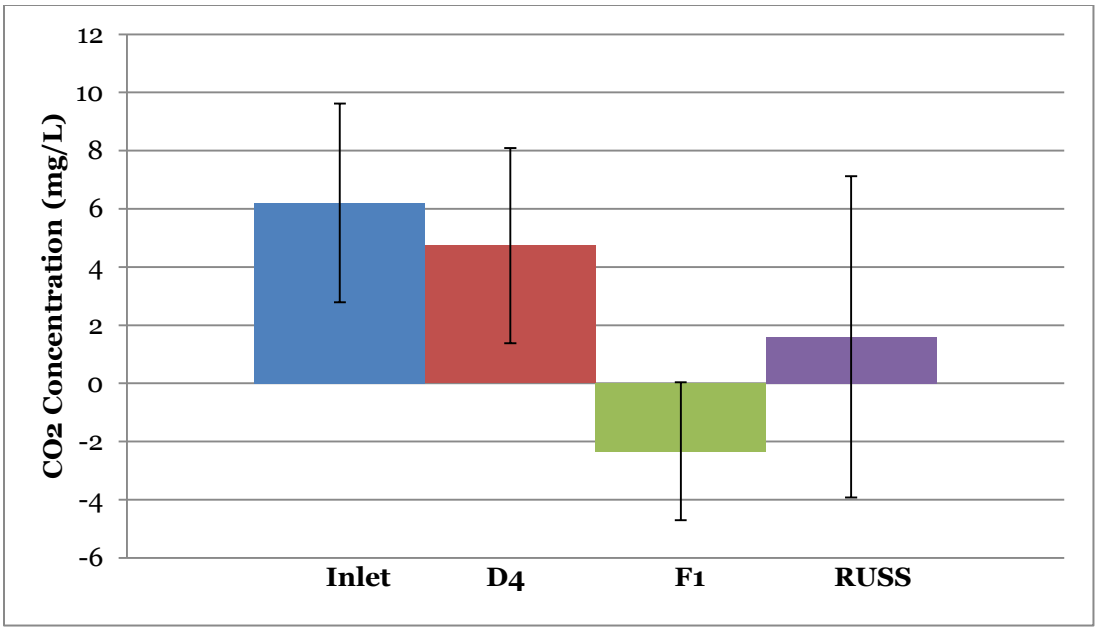

Figure 6 - Paired diel CO2 data (acidified) was averaged for each of the four sampling locations. Concentration is reported in mg/L. Error bars displayed represent one standard error (SE) above and below the average.

Conversely, however, the ambient diel difference (Figure 7) results in a negative change in carbon dioxide at the Inlet location. Both methods do agree that there is a large exchange of carbon dioxide at the D4 sampling location.

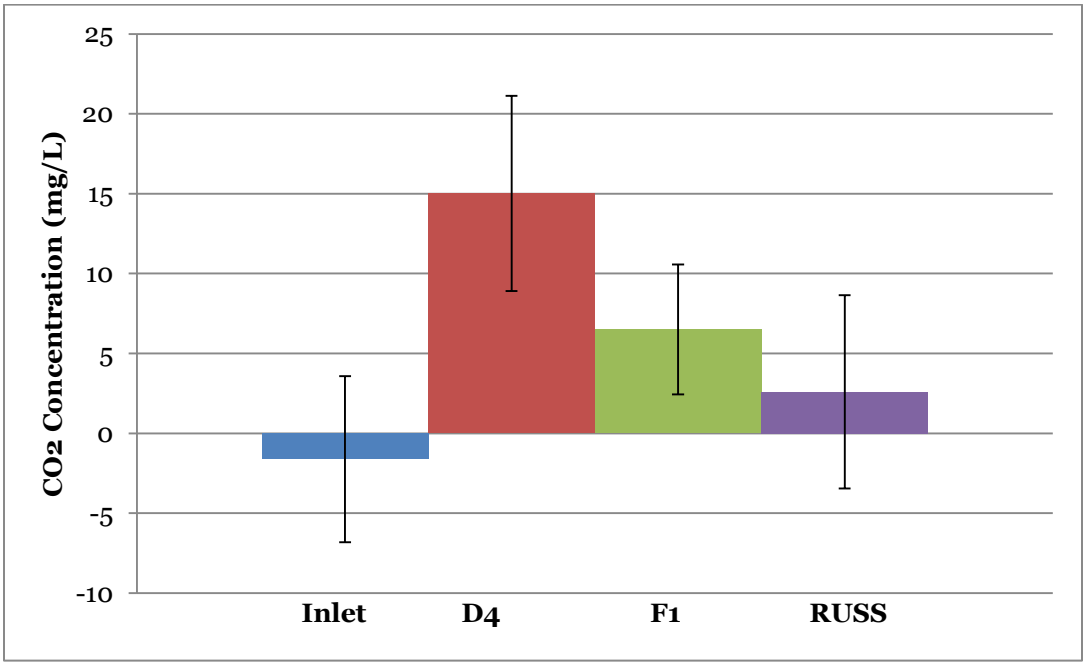

Figure 7 –Paired diel CO2 data (ambient) was averaged for each of the four sampling locations. Concentration is reported in mg/L. Error bars display represent one SE above and below the average.

An average diel dissolved oxygen concentration was found for all four sampling sites as well. As seen in Figure 8, the two largest diel DO differences are found at the Inlet and D4 sampling locations, which supports the data found by the acidified concentration.

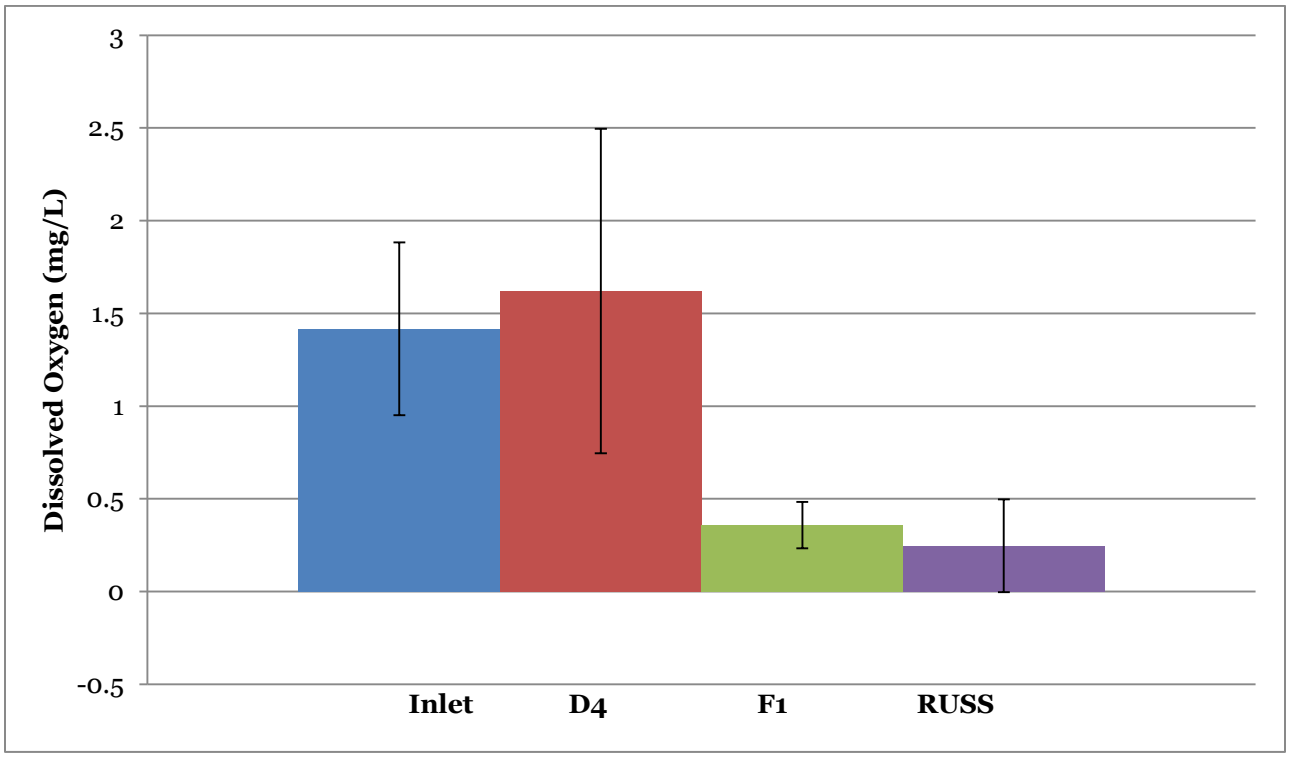

Figure 8 – Paired diel DO data was averaged for each of the four sampling locations. Concentration is reported in mg/L. Error bars display represent one SE above and below the average.

Productivity Analysis

One objective of this study was to determine the primary production of Cayuga Lake. Many studies focus on the light/dark bottle method, with ^{14}C isotope assimilation. However, with the advancing technology of dissolved oxygen probes, more studies are focusing on direct estimates of productivity from *in situ* DO measurements. The change in DO during a diel period is due to two processes: net ecosystem production (NEP) and diffusive exchange with the atmosphere (Cole, 2000).

This DO-based method predicted that the highest estimate of NEP would be at the Inlet sampling location (Figure 9). It also estimated positive productivity values at the F1 and RUSS locations. Interestingly, this model predicted a large negative productivity at the D4 sampling location. The average diel DO data for D4 was based only on two sampling dates. If these two dates were extreme events at D4, this could alter the overall estimate of NEP. Additionally, D4 has the highest DO measurements of any of the other sampling locations. The D4 location is characterized by having a high

density of macrophytes, some of which are CAM plants. Unlike traditional C3 plants, CAM plants take up CO_2 during the night where it is fixed to organic acids. This adaptation could potentially explain the negative NEP found at this sampling location, but the exact role it plays is unclear.

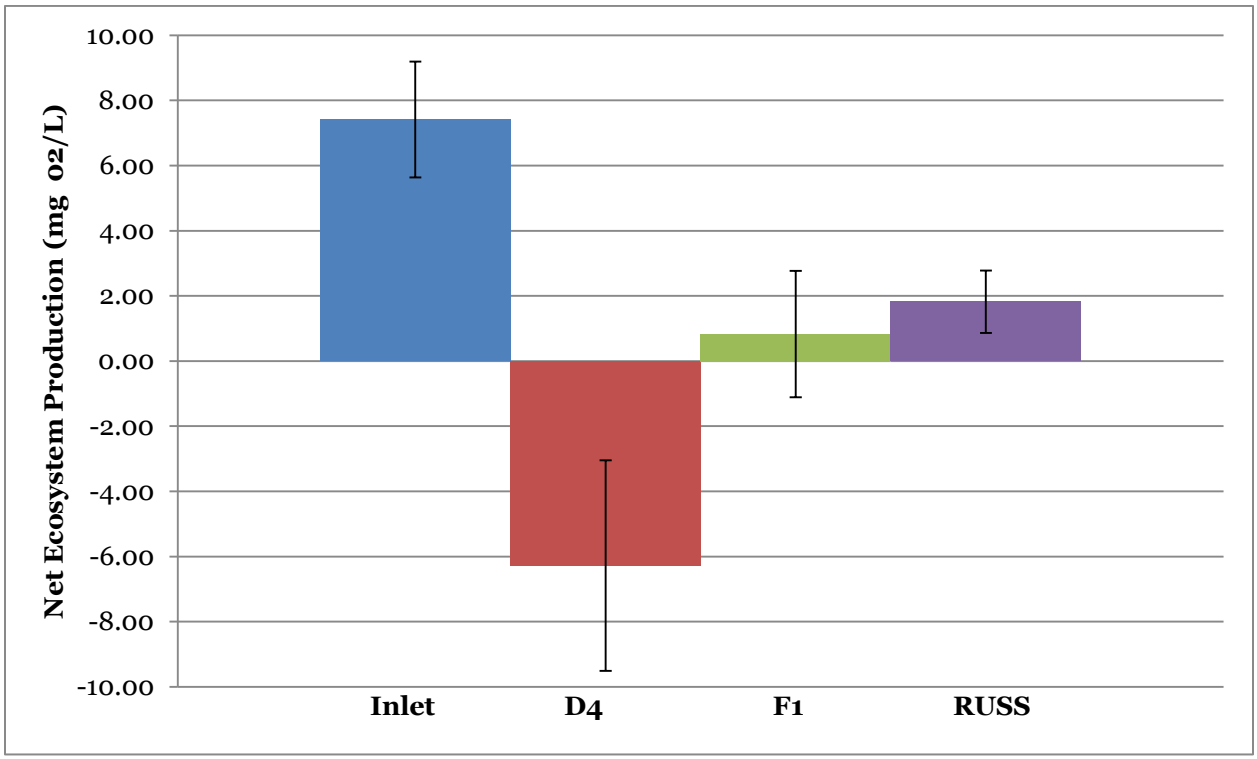

Figure 9 - Estimated net ecosystem production of the four sampling sites in Cayuga Lake based on paired diel DO measurements. Calculations are based on the methods discussed in Swaney (1999) and Cole (2000), found in Appendix II.

To accurately compare the CO_2 method to the NEP values calculated above, only the three sampling dates for which DO data were available was used. The CO_2 method assumed that diel difference in concentrations provided a direct estimate of NEP (Figures 10 & 11).

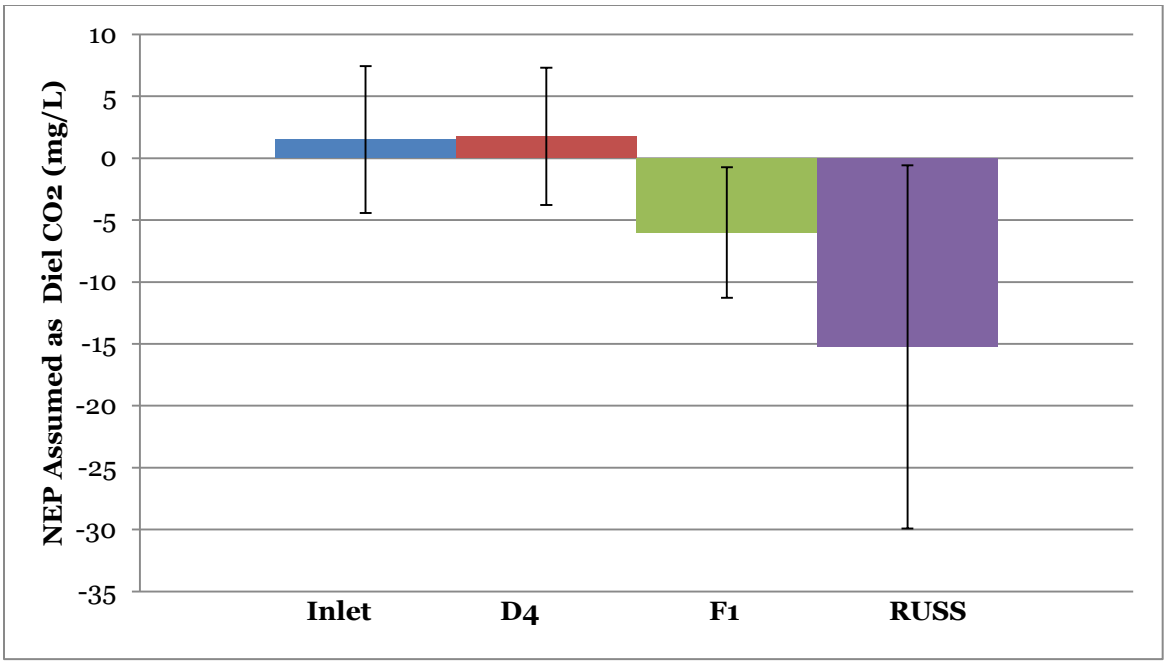

Figure 10 – NEP is assumed to be analogous to averaged paired diel CO2 data (acidified) for each of the four sampling locations on the sampling dates August 2, 1012, September 13, 2012, and September 25, 2012. Concentration is reported in mg/L. Error bars display represent one SE above and below the average.

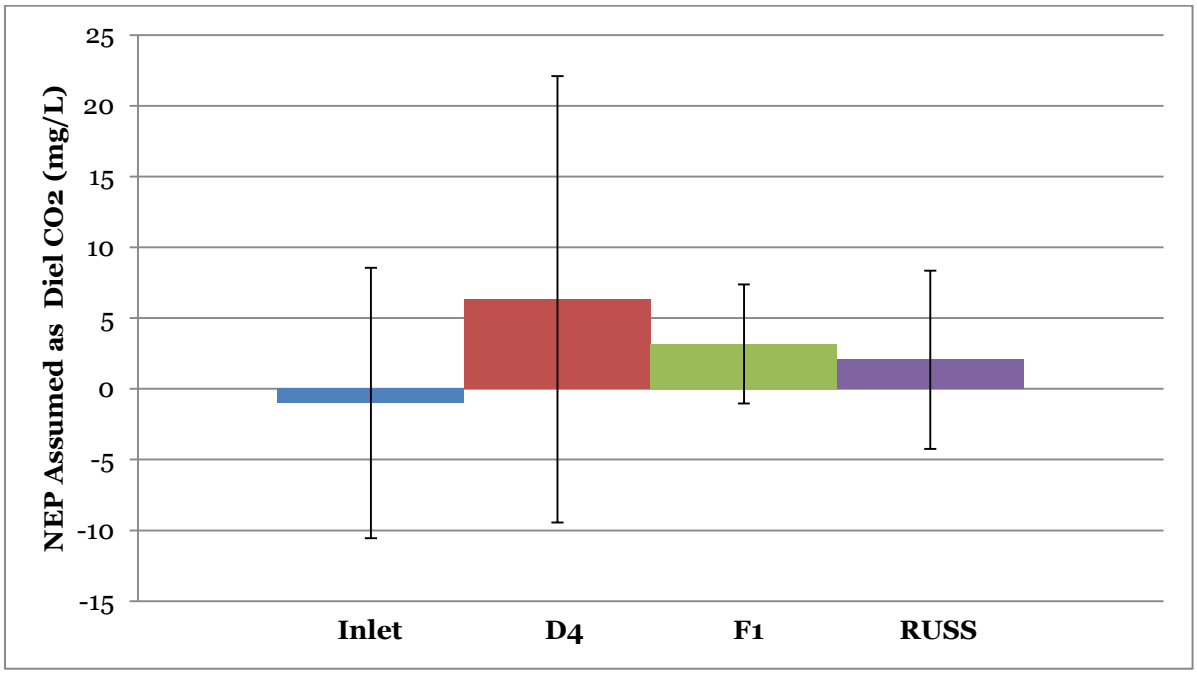

Figure 11 - NEP is assumed to be analogous to averaged paired diel CO2 data (ambient) for each of the four sampling locations on the sampling dates August 2, 1012, September 13, 2012, and September 25, 2012. Concentration is reported in mg/L. Error bars display represent one SE above and below the average.

As discussed in the *Background* section, there should theoretically be a 1:1 molar ratio between CO_2 and O_2 as given by the general photosynthetic equation. The two models presented, however, display a much more variable molar relationship between CO_2 and O_2 (Figure 12). It is interesting to note that there is a highly correlated relationship between estimated NEP using DO measurements and CO_2 readings taken directly from the water column (r^2=0.9894), but not for the acidified CO_2 readings. The acidified readings may be more variable due to error introduced by the methodology. There could also possibly be a process that we are not accounting for in the analysis.

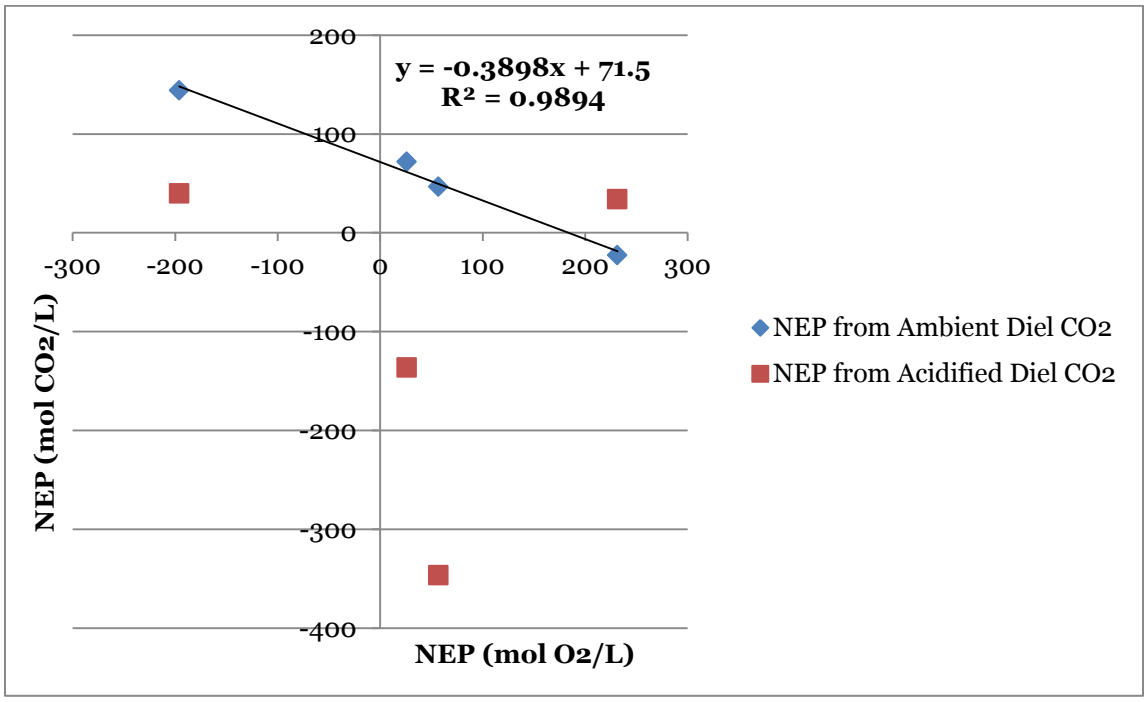

Figure 12 – A plot of molar concentrations of NEP calculated from diel O2 concentrations vs NEP calculated from diel CO2 concentrations. Although a 1:1 molar ratio is not adhered to, there is a highly correlated relationship between NEP from DO and NEP estimated from the ambient diel difference.

Future Analysis

In late April of 2013, the Ithaca Wastewater Treatment Plant deployed the YSI PISCES ecological monitoring station. The module can measure dissolved CO_2 and DO concentrations, as well as pH values and temperature readings. The equipment will collect data 24 hours a day and will post real-time data on the wastewater treatment plant's website.

The PISCES monitoring station will only measure ambient CO_2. Acidified measurements would need to be taken in the same way they were gathered for this study. Therefore, it is an important conclusion that NEP can be estimated directly from ambient CO_2 concentrations.

One of the largest issues that this study encountered was the lack of extensive data, along with the large variance in the existing dataset. With the deployment of the PISCES monitoring station, hourly measurements can be recorded. Additionally, the station will ensure that all the information gathered is complete. With a more comprehensive dataset, inherent trends and patterns will be more obvious.

Currently, there are not many studies that address the direct use of dissolved carbon dioxide measurements to determine lake metabolism. However, if real-time data are collected for an entire sampling season, a clear relationship between production estimates for DO and CO_2 may become evident.

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Appendix I

Table 1 - Aqueous acidified carbon dioxide levels. If more than one sample was taken that day at a specific location, an average is listed. Diel differences were also computed.

Date	Sampling Point	Average Morning CO_2 Concentration (mg/L)	Average Afternoon CO_2 Concentration (mg/L)	Paired Diel Difference (Morning – Afternoon) (mg/L)
7/3/2012	Inlet	87.5	89.5	-2
	D4	67	63	4
	F1	60	59	1
	RUSS	56.5	62	-5.5
7/11/2012	Inlet	82.5	84.5	-2
	D4	69.5	74	-4.5
	F1	62	79	-17
	RUSS	73.5	67.5	6
7/18/2012	Inlet	91	74	17
	D4	64	56	8
	F1	62.5	57	5.5
	RUSS	64	25	39
7/25/2012	Inlet	105.5	104	1.5
	D4	79	69	10
	F1	65	65	0
	RUSS	67	65	2
8/2/2012	Inlet	87	83	4
	D4	69	70	-1
	F1	62	75.5	-13.5
	RUSS	64	100.5	-36.5
8/30/2012	Inlet	105.5	75	30.5
	D4	86	65	21
	F1	74.5	68.5	6
	RUSS	73.5	72.5	1
9/13/2012	Inlet	52	48	4
	D4	38	32	6
	F1	38	34	4
	RUSS	36	22	14
9/25/2012	Inlet	54	60	-6
	D4	42	39	3
	F1	37	38	-1
	RUSS	35	37	-2
10/9/2012	Inlet	58	61	-3
	D4	38	51	-13
	F1	36	38	-2
	RUSS	36	36	0

Table 2 -Aqueous ambient carbon dioxide levels. If more than one sample was taken that day at a specific location, an average is listed. Diel differences were also computed.

Date	Sampling Point	Average Morning CO_2 Concentration (mg/L)	Average Afternoon CO_2 Concentration (mg/L)	Paired Diel Difference (Morning – Afternoon) (mg/L)
7/18/2012	Inlet	44	59	-15
	D4	54	32	22
	F1	37	29	8
	RUSS	49	15	34
7/25/2012	Inlet	77	88	-11
	D4	67	53	14
	F1	60	33	27
	RUSS	24	34	-10
8/2/2012	Inlet	44	64	-20
	D4	49	14	35
	F1	46	48	-2
	RUSS	44	51	-7
8/30/2012	Inlet	88	69	19
	D4	76	59	17
	F1	58	52	6
	RUSS	54	58	-4
9/13/2012	Inlet	36.5	29	7.5
	D4	26	10.83	15.16667
	F1	25	13.5	11.5
	RUSS	15.67	1.5	14.16667
9/25/2012	Inlet	3	2	1
	D4	20	0	20
	F1	2	2	0
	RUSS	1	2	-1
10/9/2012	Inlet	2	4	-2
	D4	9	27	-18
	F1	11	16	-5
	RUSS	7	15	-8

Table 3 – Dissolved oxygen levels measured using the Hydrolab DS5. If more than one sample was taken that day at a specific location, an average is listed. Diel differences were also computed.

Date	Sampling Point	Average Morning DO Concentration (mg/L)	Average Afternoon DO Concentration (mg/L)	Paired Diel Difference (Afternoon-Morning) (mg/L)
8/2/2012	Inlet	6.77	9.04	2.27
	D4	-	9.9333	-
	F1	8.21	8.4467	0.2367
	RUSS	8.305	8.5867	0.2817
9/13/2012	Inlet	7.75	9.0667	1.3167
	D4	10.135	12.63	2.495
	F1	8.05	8.62	0.57
	RUSS	7.84	8.5	0.66
9/25/2012	Inlet	6.865	7.53	0.665
	D4	9.64	10.385	0.745
	F1	9.45	9.82	0.37
	RUSS	9.095	8.89	-0.205

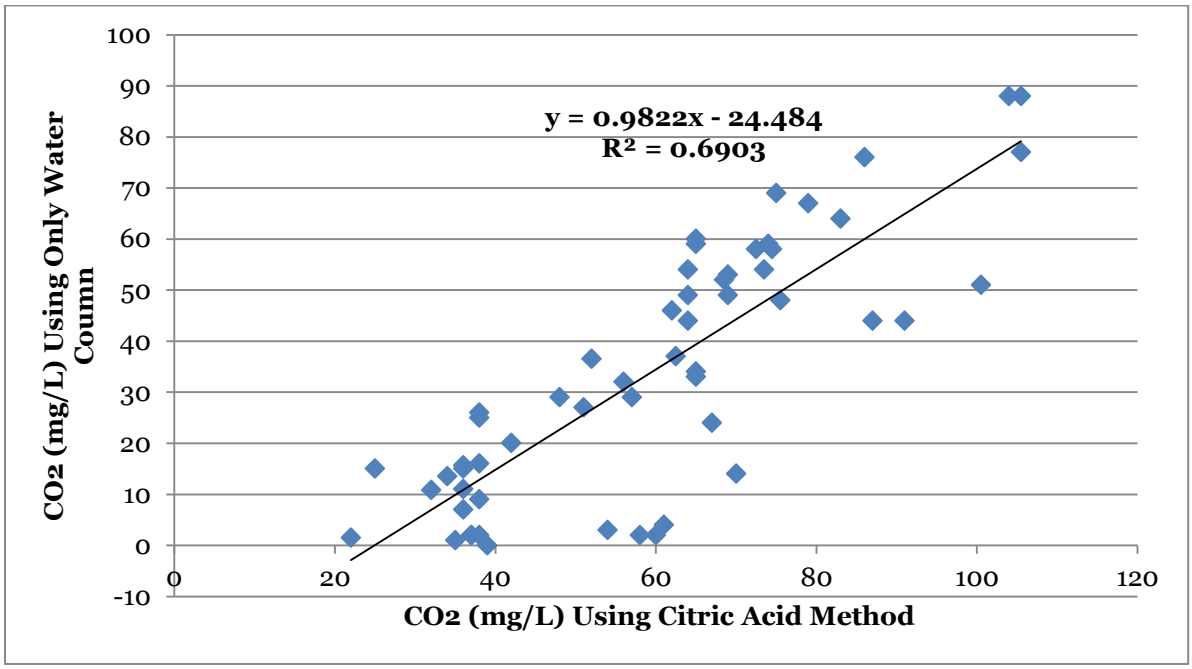

Figure 1 – Relationship between CO2 measurements as taken via the citric acid method and the water column method.

Appendix II

Estimating production from DO measurements, as adapted from Cole (2000) and Swaney (1999):

Net Ecosystem Production (NEP) can be determined by correcting the difference in DO values between two time measurements by the diffusive exchange with the atmosphere:

$$\Delta O_2 = Net\ Ecosystem\ Production \pm Diffusion$$

The diffusion term here can be either positive or negative, and is calculated by:

$$D = k(O_2 - O_{2,Sat})$$

Where O_2 is the measured oxygen concentration in the water and $O_{2,sat}$ is the oxygen concentration in the water that would be in equilibrium with the atmosphere. This is a function of temperature and altitude. In the equation above, k is the coefficient for gas exchange for O_2 at a given temperature.

MacIntyre (1995) defines k as a function of wind speed:

$$\ln(k) = 1.09 + 0.249 * V_{wind}$$

Where V_{wind} is measured in meters per second.

The diffusive correction, D, was calculated based on average values due to the limited data set. Average values for all the parameters found in the diffusion equation were found. Wind speed and temperature readings for the exact time the samples were taken were found using the Ithaca Wastewater Treatment Facility's weather station, located at N 42.4500°, W 76.5074°. Using these temperature readings, the saturated dissolved oxygen level was found, calculated at a mean altitude above sea level of 116.4 meters (Buhrer).

Table 4 - Calculations performed to estimate NEP from the Cole (2000) method

Date	Sampling Point	Avg Morning DO Conc (mg/L)	Time of Sampling	Wind Speed (mph)	Wind Speed (m/s)	k	Air Temp (F)	Air Temp (C)	O2 Sat (mg/L)	Avg Afternoon DO Conc (mg/L)	Time of Sampling	Wind Speed (mph)	Wind Speed (m/s)	k	Air Temp (F)	Air Temp (C)	O2 Sat (mg/L)	Avg D	NEP (mg/L)
8/2/2012	Inlet	6.77	6:44 AM	2.24	1.00	3.82	61.00	16.11	9.69	9.04	2:00 PM	6.11	2.73	5.87	83.60	28.67	7.68	-3.78	6.05
	D4	-	7:14 AM	4.00	1.79	4.64	63.00	17.22	9.46	9.93	2:25 PM	3.76	1.68	4.52	83.10	28.39	7.72	-	-
	F1	8.21	7:29 AM	2.42	1.08	3.89	63.12	17.29	9.45	8.45	2:43 PM	5.32	2.38	5.38	84.40	29.11	7.63	-0.98	1.22
	RUSS	8.31	7:41 AM	4.36	1.95	4.83	63.70	17.61	9.39	8.59	2:58 PM	3.07	1.37	4.18	84.20	29.00	7.64	-0.31	0.59
9/13/2012	Inlet	7.75	7:18 AM	7.45	3.33	6.82	54.83	12.68	10.44	9.07	1:19 PM	4.32	1.93	4.81	82.90	28.28	7.73	-3.93	5.25
	D4	10.14	7:49 AM	2.46	1.10	3.91	55.89	13.27	10.31	12.63	1:44 PM	6.58	2.94	6.18	83.35	28.53	7.70	12.00	-9.51
	F1	8.05	8:06 AM	4.43	1.98	4.87	56.06	13.37	10.28	8.62	2:15 PM	5.21	2.33	5.31	82.85	28.25	7.73	-3.41	3.98
	RUSS	7.84	8:24 AM	4.23	1.89	4.76	58.16	14.53	10.02	8.50	2:34 PM	2.98	1.33	4.14	83.55	28.64	7.69	-3.05	3.71
9/25/2012	Inlet	6.87	7:49 AM	3.58	1.60	4.43	59.50	15.28	9.86	7.53	1:43 PM	5.26	2.35	5.34	70.17	21.21	8.74	-10.27	10.94
	D4	9.64	8:23 AM	3.09	1.38	4.19	60.37	15.76	9.76	10.39	2:29 PM	5.01	2.24	5.20	71.18	21.77	8.65	3.79	-3.05
	F1	9.45	8:47 AM	1.39	0.62	3.47	61.09	16.16	9.68	9.82	2:50 PM	9.80	4.38	8.85	71.88	22.16	8.59	3.08	-2.71
	RUSS	9.10	9:12 AM	5.23	2.34	5.33	61.34	16.30	9.65	8.89	3:07 PM	14.23	6.36	14.50	71.58	21.99	8.61	-1.36	1.16